

METALLIC MIRROR, METALLIC ROTARY POLYGONAL MIRROR,
AND PROCESS FOR THEIR PRODUCTION

BACKGROUND OF THE INVENTION

5 Field of the Invention

This invention relates to a metallic mirror and a
metallic rotary polygonal mirror which are usable as
reflecting mirrors in copying machines, facsimile
machines, laser beam printers or the like and as
10 mirrors for microchip optical scanners, and also
relates to a process for their production. More
particularly, this invention relates to a metallic
mirror and a metallic rotary polygonal mirror which
have a superior environmental stability and a stability
15 in reflectance, having a high reflectance, and a
process for their production.

Related Background Art

Conventionally available metallic rotary polygonal
mirrors include, e.g., the following (1), (2) and (3).
20 (1) A metallic mirror whose rotary polygonal mirror
substrate made of aluminum or an aluminum alloy has
been anodized on its cut mirror surface to form a
transparent film (anodic oxide film) to provide a
mirror-surface protective film (Japanese Patent
25 Application Laid-Open No. 58-184903).
(2) A metallic mirror whose rotary polygonal mirror
substrate made of aluminum or an aluminum alloy is

provided with a metallic thin film of Cr formed by vacuum deposition and further provided thereon with a high-reflectance metallic thin film of Cu formed by vacuum deposition (Japanese Patent Application

5 Laid-Open No. 60-195502).

(3) A metallic mirror whose rotary polygonal mirror substrate made of aluminum or an aluminum alloy is provided with an intermediate layer, a metallic reflective layer and a protective film which are formed

10 by vacuum deposition in order; the intermediate layer being a Cr layer having a layer thickness of from 50 nm to 100 nm, the metallic reflective layer a Cu layer having a layer thickness of from 100 nm to 150 nm, and the protective film an Al_2O_3 layer having a layer
15 thickness of from 150 nm to 200 nm (Japanese Patent Application Laid-Open No. 6-208076).

Of the above conventional metallic mirrors, the mirror (1) has an average reflectance of about 85%, which can not be said to be a sufficient reflectance
20 for the achievement of higher speed in copying machines and laser beam printers. Also, when the anodic oxide film is formed on the substrate made of aluminum or an aluminum alloy, the presence of any impurities such as Si on the rotary polygonal mirror substrate may
25 possibly cause pit-like defects in the anodic oxide film. Accordingly, the aluminum or aluminum alloy must be those having a high purity, and hence expensive

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materials are required for the rotary polygonal mirror substrate, resulting in a high cost.

As for the mirrors (2) and (3), they have a high reflectance, but have a problem on environmental stability. When these metallic rotary polygonal mirrors are placed in a high-temperature and high-humidity environment (e.g., 45°C, 95%RH, 100 hrs, O₃ 1 ppm; or 70°C, 85%RH, 100 hrs, O₃ 1 ppm), the following phenomena may take place.

i) As shown diagrammatically in Fig. 3, dissolution reaction of metal and reduction reaction of oxygen take place, which are considered due to formation of local cells. What makes this reaction takes place is water-absorptive dust adhered to the film surface, where H₂O enters the film locally. Oxygen dissolved in the water is further involved, and the water passes from the outermost layer through SiO₂ → Al₂O₃ → Cu → Cr to reach the underlying substrate Al. As the result, an oxide of Al is formed to come into Al₂O₃, which causes volume expansion to raise the film lit, resulting in defects. This phenomenon can be explained by oxidation reduction reaction as shown by the following scheme.

Anode: $\text{Al} \rightarrow \text{Al}^3 + 3e^-$ (dissolution reaction of Al)

Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$

(reduction reaction of oxygen)

Optical-microscope photographs and a

cross-sectional photograph [analysis by FIB (focused ion beam)] of such a corrosion phenomenon are shown in Figs. 6 and 7 and Fig. 8, respectively.

More specifically, the present inventors placed in
5 the high-temperature and high-humidity environment
(45°C, 95%RH, 100 hrs, O₃ 1 ppm; or 70°C, 85%RH, 100
hrs, O₃ 1 ppm) a metallic rotary polygonal mirror
comprised of an aluminum substrate, and a Cr layer as
an intermediate layer, a Cu layer as a reflective layer
10 and an Al₂O₃ layer (dielectric layer) and an SiO₂ layer
as protective layers superposed on the aluminum
substrate, and observed it. As a result, as shown in
Figs. 6 and 7 (both optical-microscope photographs at
corroded portions) and Fig. 8 (an FIB cross-sectional
15 photograph), corrosion was found to have occurred.
ii) A phenomenon of "film lifting" may occur as shown
in a photograph 4 given as Fig. 9 and photographs 6 to
8 given as Figs. 10 to 12. As can be seen from these
cross-sectional photographs, films are separated at the
20 interface between the intermediate layer Cr film and
the reflective layer Cu film.

Measurement of each film stress between the
intermediate layer Cr, the reflective layer Cu and the
dielectric layer Al₂O₃ reveals that the Cr film has a
25 stress of $+4.15 \times 10^8$ Pa, the Cu film $+1.53 \times 10^8$ Pa,
and the Al₂O₃ film -0.63×10^8 Pa, showing great
differences in stress between them, which can be

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presumed to be caused by the separation between the Cr film and the Cu film.

SUMMARY OF THE INVENTION

5 Accordingly, an object of the present invention, which was made taking account of the problems the conventional techniques have had, is to provide a metallic mirror and a metallic rotary polygonal mirror which have a superior environmental resistance and a high reflectance, and a process for producing them.

10 Another object of the present invention is to provide a metallic mirror and a metallic rotary polygonal mirror which do not cause any phenomenon of film lifting, and a process for producing them.

15 The present invention provides a metallic mirror comprising a substrate made of aluminum or an aluminum alloy, and an intermediate layer of TiO_2 and a metallic reflective layer of Cu superposed on the substrate.

20 The present invention also provides a metallic mirror comprising a metallic polygonal mirror substrate made of aluminum or an aluminum alloy, an intermediate layer of TiO_2 formed by vacuum deposition on the substrate, a metallic reflective layer of Cu formed by vacuum deposition on the intermediate layer, and a protective layer which includes at least a layer of Al_2O_3 and is formed by vacuum deposition on the metallic reflective layer.

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The present invention also provides a process for producing a metallic mirror, comprising the steps of;

forming an intermediate layer of TiO_2 by vacuum deposition on a metallic polygonal mirror substrate comprised of aluminum or an aluminum alloy;

forming a high-reflectance metallic reflective layer of Cu by vacuum deposition on the intermediate layer; and

forming a protective layer including at least a layer of Al_2O_3 , by vacuum deposition on the metallic reflective layer.

It is considered that a good environmental stability attributable to the metallic mirror of the present invention can be explained in the following way.

A thin TiO_2 film formed as an intermediate layer between the mirror surface of rotary polygonal mirror substrate made of aluminum or an aluminum alloy and the metallic reflective layer Cu film can prevent H_2O and O_2 from entering through the film outermost layer in a high-humidity environment. As the result, the aluminum or aluminum alloy substrate can be kept from being oxidized into Al_2O_3 which brings about volume expansion to raise the film, so that corrosion damage is inhibited from occurring.

It is also considered that the advantage brought about by the metallic mirror of the present invention

which do not cause any phenomenon of film lifting can be explained in the following way.

The stress of the various thin films of Cr (stress: $+4.15 \times 10^8$ Pa), Cu (stress: $+1.53 \times 10^8$ Pa) and Al_2O_3 (stress: -0.63×10^8 Pa) has been greatly different between Cr and Cu films, whereas, in place of these, the thin films in the present invention are constituted of TiO_2 (stress: $+0.30 \times 10^8$ Pa), Cu and Al_2O_3 , so that the difference in stress between the thin films can be minimized, and the phenomenon of "film lifting" can be prevented from occurring between the Cr and Cu films.

Here, the stress is measured by the Stoney's method in which stress is determined from warpage of each film formed as a single film on a glass substrate, and is calculated from the following equation.

$$\text{Tress } \sigma = EsD^2/[6(1 - \nu)R]$$

wherein:

Es: Young's modulus of the substrate;
D: thickness of the substrate;
 ν : Poisson's ratio of the substrate; and
R: curvature of radius of warpage;
and plus sign (+) indicates tensile direction, and minus sign (-) compression direction.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a partial (about half) diagrammatic

cross-sectional illustration of metallic rotary polygonal mirrors of Examples 1 and 2 according to the present invention.

Fig. 2 is a partial (about half) diagrammatic cross-sectional illustration of metallic rotary polygonal mirrors of Examples 3 and 4 according to the present invention.

Fig. 3 is a diagrammatic illustration of a phenomenon of corrosion.

Fig. 4 is a graph showing spectral characteristics of reflectance when TiO_2 [curved line (a)] or Cr_2O_3 [curved line (b)] is used as an intermediate-layer material.

Fig. 5 is a graph making a comparison between spectral characteristics of reflectance in S polarized light at an incident angle of 15° when a TiO_2 film is used as the intermediate layer [curved line (b): double-layer protective layer; curved line (c): triple-layer protective layer] and spectral characteristics of reflectance in S polarized light at incident angle of 15° when conventional Cr is used [curved line (a)].

Fig. 6 is an optical-microscope photograph showing corrosion of an intermediate layer in a conventional case.

Fig. 7 is an optical-microscope photograph showing corrosion of an intermediate layer in a conventional

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case.

Fig. 8 is an FIB cross-sectional photograph of a corroded portion.

Fig. 9 is an FIB cross-sectional photograph of a phenomenon of film lifting.

Fig. 10 is a surface optical-microscope photograph of the phenomenon of film lifting.

Fig. 11 is a surface optical-microscope photograph of the phenomenon of film lifting.

Fig. 12 is a surface optical-microscope photograph of the phenomenon of film lifting.

Fig. 13 is an SEM (scanning electron microscope) photograph of a Cr film surface.

Fig. 14 is an SEM (scanning electron microscope) photograph of a TiO_2 film surface.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The metallic mirror of the present invention is usable as various types of mirrors such as a bathroom mirror, an automobile rearview mirror, a lamp reflecting mirror and a dentist's mirror. Fig. 1 shows an example in which the metallic mirror according to the present invention is used as a rotary polygonal mirror.

As shown in Fig. 1, on the periphery of a rotary polygonal mirror substrate 1 made of aluminum or an aluminum alloy, a mirror surface is formed by cutting

or the like. Here is shown an example of an octahedral metallic rotary polygonal mirror, which, however, may be polygonal other than octahedral.

Such a mirror has an insufficient reflectance of about 86% in itself, and also the substrate can not be said to have a sufficient corrosion resistance. Accordingly, in the present invention, an intermediate layer formed of TiO_2 and a metallic reflective layer 3 formed of Cu are provided on this metallic polygonal mirror substrate 1. The Cu metallic reflective layer 3 has a higher reflectance than the substrate metal (i.e., aluminum or an aluminum alloy). This can make higher the reflectance required as a metallic rotary polygonal mirror. In the present invention, the TiO_2 intermediate layer 2 is provided so that the mirror surface of the substrate metal can be prevented from corrosion and the adhesion between the substrate and the high-reflectance metallic reflective layer can be improved.

In the present invention, the intermediate layer formed of TiO_2 may usually have a thickness of from 20 nm to 200 nm, preferably from 50 nm to 150 nm, and most preferably from 50 nm to 100 nm, because a too thin layer may have an insufficient durability and a too thick layer takes a long time for its formation, resulting in a poor productivity. In the present invention, the layer thickness refers to mechanical

layer thickness unless otherwise specified.

The metallic reflective layer formed of Cu may also usually have a thickness of 80 nm or larger, preferably from 80 nm to 150 nm, and most preferably
5 from 80 nm to 100 nm, because a too thin layer may have an insufficient reflectance and a too thick layer takes a long time for its formation, resulting in a poor productivity.

The TiO_2 intermediate layer and Cu metallic
10 reflective layer may preferably be formed by, but not particularly limited to, deposition. This deposition includes vacuum deposition (in a narrow sense), sputtering and ion plating. With regard to the Cu film, it may be formed by a wet process such as
15 plating, but in usual cases the deposition is preferred.

In the present invention, for the purpose of protecting the mirror surface and further for the purpose of also enhancing reflection, a protective
20 layer which is comprised of one or more layers may preferably be provided on the surface of the metallic reflective layer. This protective layer is usually formed of a transparent dielectric material. In order to improve the function of protection or in order to
25 enhance reflection more effectively, the protective layer may be of a multiple layer. In particular, it is preferred that a protective layer is alternately formed

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of, from the metallic reflective layer side, a dielectric material having a low refractive index and a dielectric material having a high refractive index because a high reflectance can be easily achieved.

5 The dielectric material having a low refractive index may include MgF_2 , SiO_2 and Al_2O_3 . As the dielectric material having a high refractive index, ZrO_2 , TiO_2 , CeO_2 and SiO are preferred. Also, in this case, each protective layer may preferably have a layer
10 thickness which is so optimized as to maximize a reflectance at the desired wavelength and minimize dependence upon an angle of incident light.

 The intermediate layer TiO_2 film is indispensable in order to improve the adhesion between the substrate
15 metal and the high-reflectance metallic reflective layer thin film. This is the most important item in the present invention.

 The present invention will be described below by giving Examples. Fig. 1 is a partial (about half)
20 diagrammatic cross-sectional illustration of metallic rotary polygonal mirrors of Examples 1 and 2 according to the present invention. Fig. 2 is a partial (about half) diagrammatic cross-sectional illustration of metallic rotary polygonal mirrors of Examples 3 and 4
25 according to the present invention.

Example 1

As shown in Fig. 1, on the metallic polygonal

mirror substrate 1 made of an aluminum alloy (Al-Mg type), the intermediate layer 2, the metallic reflective layer 3, a protective layer (first protective layer) 4 and a protective layer (second protective layer) 5 were formed in order.

The intermediate layer 2 is a TiO_2 film, which may have a layer thickness of from 50 nm to 150 nm. If it has a thickness smaller than 50 nm, durability is insufficient. If it has a thickness larger than 150 nm, it takes a long time for deposition, resulting in a poor productivity.

When the intermediate layer comprised of this TiO_2 film is formed by vacuum deposition, the film may preferably be formed adding an O_2 gas under a pressure of from 6.65×10^{-3} Pa to 26.6×10^{-3} Pa (5×10^{-5} Torr to 2×10^{-4} Torr) as total pressure in the reaction space. If the O_2 gas pressure is lower than 6.65×10^{-3} Pa, it is considered that the underlying aluminum alloy have a poor affinity for the TiO_2 film, so that film separation tends to occur between the TiO_2 film and the Cu film. If on the other hand it is higher than 26.6×10^{-3} Pa, it is considered that the Cu film tends to be oxidized, so that the mirror may have a reflectance lower than the desired 95%. Accordingly, the O_2 added in order to prevent film separation while ensuring the desired reflectance of 95% or higher may preferably be at the pressure of from 6.65 to 26.6×10^{-3} Pa.

The metallic reflective layer 3 is a Cu film, which may have a layer thickness of from 80 nm to 150 nm. If the Cu film has a layer thickness smaller than 80 nm, a low reflectance may result. If it has a thickness larger than 150, it takes a long time for deposition, resulting in a poor productivity. The metallic reflective layer 3 is formed using a W (tungsten) boat resistance heating system as an evaporation material heating system.

When the high-reflectance metallic thin film of Cu is formed by vacuum deposition on the intermediate layer of TiO_2 film, it may preferably be formed after the inside of a vacuum deposition chamber reaches a degree of vacuum of 2.66×10^{-3} (2×10^{-5} Torr) Pa or above subsequently to the formation of the intermediate layer of TiO_2 film. If the inside of a vacuum deposition chamber has a degree of vacuum lower than 2.66×10^{-3} Pa, the mirror may have a reflectance lower than the desired 95%. On the other hand, a reflectance of the desired 95% or higher can be ensured when the Cu film is formed by vacuum deposition after the pressure has come to be 2.66×10^{-3} Pa or above. This is presumed as follows: Any excess gas components remaining in the vacuum deposition chamber can be made less when the chamber is brought into a high vacuum state before the deposition of Cu film, so that any residual gas can be prevented from entering the Cu film

(to cause its oxidation), hence a Cu film with a high quality can be formed and the high reflectance can be ensured.

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The protective layer (first protective layer) 4 is
5 comprised of an Al_2O_3 film, and may have a layer
thickness of from 150 nm to 200 nm. If the Al_2O_3 film
has a layer thickness smaller than 150 nm, durability
may be insufficient. If it has a layer thickness
larger than 200 nm, the mirror may have insufficient
10 optical characteristics such as reflecting properties
inclusive of incident-angle dependence.

When the protective layer of Al_2O_3 is formed by
vacuum deposition on the high-reflectance metallic thin
film of Cu, the protective layer or film may preferably
15 be formed by vacuum deposition i) without addition of
any O_2 gas at the initial stage of film formation until
the film comes to have a layer thickness of 15 to 30%
of the stated layer thickness, in order to improve the
affinity of the Al_2O_3 protective film for the Cu film,
20 in other words, the former's adhesion to the latter,
and ii) further thereon, after the film has been formed
beyond 15 to 30% and until it comes to have the stated
layer thickness, with addition of O_2 gas so that almost
all the film has an Al:O ratio of 2:3, i.e., the film
25 of Al_2O_3 sufficiently combined with oxygen. Even when
the film is formed by vacuum deposition with addition
of O_2 gas from beginning to end of the film formation,

there is no problem in both reflectance and adhesion. The value of reflectance can be made higher by about 0.3 to 0.5% when as described above the film is formed by vacuum deposition without addition of any O_2 gas at the initial stage of film formation until the film comes to have a layer thickness of 15 to 30% of the stated layer thickness and further thereon with addition of O_2 gas after the film has been formed beyond 15 to 30% and until it comes to have the stated layer thickness.

This is presumed as follows: Where the O_2 gas is fed into the vacuum deposition chamber in order to form the protective layer of Al_2O_3 after the high-reflectance metallic thin film of Cu has been formed, the surface layer portion of the Cu film may undergo oxidation to result in a little low reflectance though the desired reflectance of 95% can be ensured, whereas the addition of no O_2 gas at the initial stage of film formation until the film comes to have a layer thickness of 15 to 30% of the stated layer thickness prevents the Cu film surface layer portion from being oxidized, so that the reflectance can be at a higher value. However, unless the O_2 gas is added after the film has been formed beyond 30%, though there is no problem on the reflectance, the film lifting may occur. Accordingly, the formation of the Al_2O_3 film without addition of any O_2 gas may be only at the initial stage of film

formation during which the film comes to have a layer thickness of 15 to 30% of the stated layer thickness. Also, the amount of O_2 gas added when the Al_2O_3 film is deposited, i.e., the total pressure of reaction space that is substantially determined by the O_2 gas fed into the chamber may be within the range of from 6.65×10^{-3} Pa to 26.6×10^{-3} Pa taking account of any occurrence of film separation. The film of Al_2O_3 can be formed even without addition of O_2 gas when the Al_2O_3 film is formed. This is because oxygen atoms are contained in materials other than the O_2 gas and such materials are used in film formation.

The protective layer (second protective layer) 5 is an SiO_2 film, which may have a layer thickness of from 10 nm to 20 nm. If it has a layer thickness smaller than 10 nm, it may provide a low surface strength. If it has a layer thickness larger than 20 nm, the mirror may have insufficient optical characteristics such as reflecting properties.

Conditions for forming the respective films in Example 1 are shown in Table 1.

Example 2

In Example 2, on the metallic polygonal mirror substrate 1 made of an aluminum alloy (Al-Mg type), an intermediate layer 2, a metallic reflective layer 3, a protective layer (first protective layer) 4 and a protective layer (second protective layer) 5 were

formed in order. The intermediate layer 2, the metallic reflective layer 3, the protective layer (first protective layer) 4 and the protective layer (second protective layer) 5 were formed in the same manner as in Example 1 except that the metallic reflective layer 3 was formed by employing a deposition material heating system making use of electron beams.

Conditions for forming the respective films in Example 2 are shown in Table 2.

As can be seen from Tables 1 and 2, Examples 1 and 2 differ in the deposition material heating system for forming the metallic reflective layer. In Example 1, W (tungsten) boat resistance heating is used, but in Example 2 electron beams are used.

Example 3

In Example 3, as shown in Fig. 2, on a metallic polygonal mirror substrate 1 made of an aluminum alloy (Al-Mg type), an intermediate layer 2, a metallic reflective layer 3, a protective layer (first protective layer) 4, a protective layer (second protective layer) 5 and a protective layer (third protective layer) 6 were formed in order. In Example 3, differently from Examples 1 and 2, a third protective layer is provided on the second protective layer. Also, in Example 3, the metallic reflective layer 3 was formed by employing W boat resistance heating as the deposition material heating system in

the same manner as in Example 1. The intermediate layer 2, the metallic reflective layer 3 and the protective layer (first protective layer) 4 were also formed in the same manner, and details on these are omitted here accordingly.

The protective layer (second protective layer) 5 is comprised of a TiO_2 film, and may have a layer thickness of from 80 nm to 100 nm. If it has a layer thickness smaller than 80 nm or larger than 100 nm, the mirror may have insufficient optical characteristics such as reflecting properties inclusive of incident-angle dependence.

The protective layer (third protective layer) 6 is an SiO_2 film, which may have a layer thickness of from 10 nm to 20 nm. If it has a layer thickness smaller than 10 nm, it may provide a low surface strength. If it is in a thickness larger than 20 nm, the mirror may have insufficient optical characteristics such as reflecting properties.

Conditions for forming the respective films in Example 3 are shown in Table 3.

Example 4

In Example 2, on the metallic polygonal mirror substrate 1 made of an aluminum alloy (Al-Mg type), an intermediate layer 2, a metallic reflective layer 3, a protective layer (first protective layer) 4, a protective layer (second protective layer) 5 and a

protective layer (third protective layer) 6 were formed in order. The intermediate layer 2, the metallic reflective layer 3, the protective layer (first protective layer) 4, the protective layer (second protective layer) 5 and the protective layer (third protective layer) 6 were formed in the same manner as in Example 3 except that the metallic reflective layer 3 was formed by employing a deposition material heating system making use of electron beams.

Conditions for forming the respective films in Example 4 are shown in Table 4.

As can be seen from the accompanying Tables 3 and 4, Examples 3 and 4 differ in the deposition material heating system for forming the metallic reflective layer. In Example 3, W (tungsten) boat resistance heating is used, but in Example 4 electron beams are used.

With regard to the above Examples 1 to 4;

summarized in Table 5 is the relationship between

i) the amount of O_2 gas added during deposition of the intermediate layer TiO_2 , in other words, the total pressure of reaction space when the O_2 is added, ii) reflectance before and after a durability test (left standing under the conditions shown in the table) and iii) adhesion of the Cu film to the TiO_2 film;

in Table 6, the relationship between i) degree of vacuum during deposition of the metallic reflective

layer Cu film and ii) reflectance before and after the durability test;

in Table 7, the relationship between i) layer thickness by which the O_2 gas is not added at the
5 initial stage of deposition of the protective layer Al_2O_3 film, ii) reflectance before and after the durability test and iii) adhesion of the Al_2O_3 film to the Cu film; and

in Table 8, the relationship between i) the amount
10 of O_2 gas added during deposition of the protective layer Al_2O_3 film, in other words, the total pressure of reaction space when the O_2 is added and ii) adhesion of the Al_2O_3 film to the Cu film.

In these tables, as to "A" and "C" shown as
15 evaluation results in the item "adhesion", "A" is a symbol indicating that film separation does not occur, and "C", film separation occurs.

Also summarized in Table 9 are the results of evaluation on corrosion percentage after durability
20 test, reflectance, film lifting percentage, adhesion, and wiping resistance.

As can be seen from Table 5, the film separation is seen to have occurred when the amount of O_2 gas added during deposition of the intermediate layer TiO_2 , in
25 other words, the total pressure of reaction space when the O_2 is added is below 6.65×10^{-3} Pa (0.5×10^{-4} Torr in Table 5). As also can be seen from Table 6, in the

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state the degree of vacuum during deposition of the Cu film is below 3.32×10^{-3} Pa (2.5×10^{-5} Torr), the reflectance is lower than 95% in some cases depending on wavelength. As still also can be seen from Table 7, the film separation is seen to have occurred when the layer thickness formed while the O_2 gas is not added from the beginning of deposition of the protective layer Al_2O_3 film is larger than 30% of the stated layer thickness (e.g., a layer thickness of 38%). As further can be seen from Table 8, the film separation is seen to have occurred when the amount of O_2 gas added during deposition of the protective layer Al_2O_3 film, in other words, the total pressure of reaction space is outside the range of from 6.65×10^{-3} Pa to 26.6×10^{-3} Pa. As still further can be seen from Table 9, both the adhesion and the wiping resistance are good in Examples 1 to 4.

To test the adhesion, a pressure-sensitive adhesive tape (available from Nichiban Co., Ltd.) was brought into close adhesion to the surface of the metallic rotary polygonal mirror, and then peeled therefrom at a rate of 20 mm/sec to visually examine whether or not the surface has peeled.

To test the wiping resistance, a sheet of lens cleaning paper (Dusper was used) was impregnated with a solvent (50 vol.% of ether + 50 vol.% of methanol). This cleaning paper was pressed against the metallic

rotary polygonal mirror at a pressure of 2 kg/cm², and moved back and forth ten times, and thereafter, visual examination was made on whether or not any scratches are seen at the surface. In Table 9, "A" indicates that the surface was not scratched even by the wiping resistance test.

Comparative Test

As shown in Tables 10 and 11, films of various materials Cr, Ni, Ti, Ni-Cr (Cr: 20 wt.%), Cr₂O₃ (with O₂), Cr₂O₃ (without O₂), ZrO₂ (with O₂), Al₂O₃ (without O₂), SiO₂ (with O₂), Ta₂O₅ (without O₂) and TiO₂ (with O₂) were each formed by vacuum deposition in a layer thickness of 80 nm to 120 nm.

("With O₂" shows that the film was deposited in an atmosphere with addition of O₂ at an O₂ partial pressure of 1.99×10^{-3} Pa.)

On each film thus formed, a thin film of Cu was superposed in a thickness of about 100 nm, and on the thin film of Cu an Al₂O₃ film was further formed in a thickness of 170 nm. Then as the outermost surface layer an SiO₂ film was formed in a thickness of 14 nm. The Al₂O₃ and SiO₂ films were formed at an O₂ partial pressure of 1.99×10^{-3} Pa.

Metallic rotary polygonal mirrors thus obtained were left standing in an atmosphere of 70°C, 85%RH and O₃ concentration of 1 ppm for 100 hours to examine their environmental properties. Layer configuration:

Al/intermediate layer/Cu/Al₂O₃/SiO₂.

With regard to "Corrosion" in Table 10, even slight changes of mirror surface in appearance before and after the durability test were counted as the number of occurrence.

As the result, as shown in Tables 10 and 11, the following is seen.

- (1) The adhesion of the metallic reflective layer to the substrate material satisfies the standard except for the sample having no intermediate layer.
- (2) With regard to the corrosion, when examined by the method in which even slight changes of mirror surface in appearance before and after the durability test are counted as the number of occurrence, corrosion percentages are 10% or less in three types, Ni-Cr (Cr: 20 wt.%), Cr₂O₃ (with O₂) and TiO₂ (with O₂).
- (3) When the reflectance at an incident angle 15° of S polarized light with wavelength of 655 nm, 675 nm and 780 nm each is examined before and after the durability test, almost all samples having the intermediate layers except for the TiO₂ film do not satisfy the standard of 95% or higher.
- (4) With regard to the phenomenon of film lifting, oxide type intermediate layer materials are more effective for preventing its occurrence than metal type ones.

With regard to Cr₂O₃ (with O₂), showing good

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results on the above-(2) corrosion, the reflectance is not sufficient from the initial stage. Fig. 4 shows spectral characteristics of reflectance in respect of TiO_2 [curved line (a)] or Cr_2O_3 [curved line (b)]. As shown therein, the Cr_2O_3 results in an insufficient reflectance. With regard to Ni-Cr (Cr: 20 wt.%), showing good results on the above-(2) corrosion, there is a little problem on the phenomenon of film lifting and further there is another problem that the film formation speed is so low as to be not suitable for production.

In Fig. 5, spectral characteristics of reflectance in S polarized light at an incident angle of 15° are compared between when the TiO_2 film is used as the intermediate layer [curved line (b): double-layer protective layer; curved line (c): triple-layer protective layer) and when the conventional Cr is used [curved line (a)]. As can be seen therefrom, a reflectance comparable to or higher than conventional cases is obtainable also when the TiO_2 film is used as the intermediate layer.

To make sure that the TiO_2 film is superior as the intermediate layer, the state of film surface of each of the TiO_2 thin film and the Cr thin film was observed on an FESEM (field emission scanning electron microscope). The film surface of the Cr thin film is, as shown in Fig. 13, seen to have a columnar texture,

and supposed to allow H_2O and O_2 to pass, whereas, as shown in Fig. 14, that of the TiO_2 thin film has a dense film structure, and is presumed to be able to prevent H_2O and O_2 from entering.

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Table 1

Layers	Deposition material heating	Substrate temperature (°C)	Degree of vacuum (Torr)	Deposition rate (mm/sec)
Intermediate layer 2:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
Metallic reflecting layer 3:	W boat resistance heating	150	1.0×10^{-5}	2.0
Protective layer 4:	Electron beams	150	1.5×10^{-4} O ₂ added*	0.2
Protective layer 5:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2

* But without addition of O₂ at the initial stage of film formation until the film came to have a layer thickness of 15 to 30% of the stated layer thickness.

Table 2

Layers	Deposition material heating	Substrate temperature (°C)	Degree of vacuum (Torr)	Deposition rate (mm/sec)
Intermediate layer 2:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
metallic reflecting layer 3:	Electron beams	150	1.0×10^{-5}	2.0
Protective layer 4:	Electron beams	150	1.5×10^{-4} O ₂ added*	0.2
Protective layer 5:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2

* But without addition of O₂ at the initial stage of film formation until the film came to have a layer thickness of 15 to 30% of the stated layer thickness.

Table 3

Layers	Deposition material heating	Substrate temperature (°C)	Degree of vacuum (Torr)	Deposition rate (mm/sec)
Intermediate layer 2:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
Metallic reflecting layer 3:	W boat resistance heating	150	1.0×10^{-5}	2.0
Protective layer 4:	Electron beams	150	1.5×10^{-4} O ₂ added*	0.2
Protective layer 5:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
Protective layer 6:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2

Table 4

Layers	Deposition material heating	Substrate temperature (°C)	Degree of vacuum (Torr)	Deposition rate (mm/sec)
Intermediate layer 2:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
Metallic reflecting layer 3:	Electron beams	150	1.0×10^{-5}	2.0
Protective layer 4:	Electron beams	150	1.5×10^{-4} O ₂ added*	0.2
Protective layer 5:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2
Protective layer 6:	Electron beams	150	1.5×10^{-4} O ₂ added	0.2

(In Tables 3 & 4) * But without addition of O₂ at the initial stage of film formation until the film came to have a layer thickness of 15 to 30% of the stated layer thickness.

Table 5

Amount of O ₂ gas added during deposition of intermediate layer TiO ₂ (×10 ⁻⁴ Torr)		Reflectance (S polarized light)					Adhe- sion	
		Before durability test		After durability test				
		655 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)		
0.0	Example 1:	96.2	96.3	97.2	96.1	96.3	97.2	C
	Example 2:	95.3	95.9	96.9	95.2	95.8	96.8	C
	Example 3:	97.2	97.6	98.0	97.0	97.2	97.6	C
	Example 4:	97.1	97.7	98.0	96.9	97.4	97.8	C
0.3	Example 1:	96.3	96.7	97.5	96.1	96.5	97.3	C
	Example 2:	95.5	96.0	97.0	95.3	96.0	96.9	C
	Example 3:	97.2	97.5	98.1	97.0	97.4	97.8	C
	Example 4:	97.4	97.9	98.4	97.1	97.8	98.2	C
0.5	Example 1:	96.4	96.7	97.5	96.2	96.5	97.4	A
	Example 2:	95.4	96.0	97.1	95.2	95.8	97.0	A
	Example 3:	97.3	97.7	98.4	97.1	97.6	98.3	A
	Example 4:	97.4	98.0	98.5	97.2	97.8	98.3	A
1.0	Example 1:	96.6	96.7	97.6	96.5	96.7	97.7	A
	Example 2:	95.6	96.1	97.2	95.4	96.0	97.1	A
	Example 3:	97.4	97.8	98.5	97.2	97.6	98.3	A
	Example 4:	97.5	98.0	98.7	97.3	97.8	98.7	A
1.2	Example 1:	96.3	96.8	97.6	96.1	96.7	97.4	A
	Example 2:	95.5	96.0	97.0	95.3	96.3	97.7	A
	Example 3:	97.5	97.9	98.5	97.4	97.8	98.4	A
	Example 4:	97.6	98.0	98.7	97.4	97.9	98.6	A

Degree of vacuum before deposition of Cu: 1.0×10^{-5} Torr.
O₂ gas (1.5×10^{-4} Torr) added throughout deposition of Al₂O₃.
Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 5 (Cont'd)

Amount of O ₂ gas added during deposition of intermediate layer TiO ₂ ($\times 10^{-4}$ Torr)	Reflectance (S polarized light)						Adhesion	
	Before durability test		After durability test					
	655 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)			
1.5	Example 1:	96.1	96.3	97.2	96.0	96.3	97.2	A
	Example 2:	95.5	96.1	97.1	95.4	96.3	97.7	A
	Example 3:	97.5	98.0	98.6	97.3	97.8	98.5	A
	Example 4:	97.7	98.2	98.8	97.5	98.1	98.7	A
2.0	Example 1:	95.5	96.0	97.0	95.3	95.7	96.7	A
	Example 2:	95.4	95.8	96.8	95.2	95.6	96.6	A
	Example 3:	95.9	97.6	98.4	95.7	97.4	98.2	A
	Example 4:	96.7	97.9	98.2	96.5	97.7	98.0	A
2.5	Example 1:	94.4	95.3	96.7	93.9	94.9	95.8	A
	Example 2:	94.2	95.2	96.4	93.7	94.6	95.9	A
	Example 3:	95.0	96.8	97.5	94.8	96.1	96.9	A
	Example 4:	95.0	96.7	97.4	94.7	96.4	96.9	A

Degree of vacuum before deposition of Cu: 1.0×10^{-5} Torr.O₂ gas (1.5×10^{-4} Torr) added throughout deposition of Al₂O₃.

Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 6

Degree of vacuum during deposition of Cu ($\times 10^{-5}$ Torr)	Reflectance (S polarized light)						
	Before durability test		After durability test				
	655 nm (%)	675 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)	
0.5	Example 1:	96.4	96.6	97.5	96.3	96.5	97.4
	Example 2:	95.9	96.2	97.1	95.8	96.1	97.0
	Example 3:	97.6	98.2	98.6	97.5	98.1	98.5
	Example 4:	97.6	98.0	98.8	97.3	97.9	98.5
0.8	Example 1:	96.3	96.5	97.5	96.2	96.4	97.4
	Example 2:	95.9	96.3	97.2	95.8	96.2	97.1
	Example 3:	97.5	98.1	98.7	97.4	98.0	98.6
	Example 4:	97.7	98.1	98.8	97.5	98.0	98.6
1.0	Example 1:	96.1	96.3	97.2	96.0	96.3	97.2
	Example 2:	95.5	96.1	97.1	95.4	96.3	97.7
	Example 3:	97.5	98.0	98.6	97.3	97.8	98.5
	Example 4:	97.7	98.2	98.8	97.5	98.1	98.7
1.5	Example 1:	96.0	96.2	97.0	95.8	96.0	96.9
	Example 2:	95.5	96.0	97.2	95.4	96.2	97.1
	Example 3:	97.4	98.0	98.5	97.3	97.9	98.4
	Example 4:	97.6	98.2	98.7	97.5	98.0	98.5
2.0	Example 1:	95.8	96.0	96.8	95.7	96.0	96.6
	Example 2:	95.3	95.9	97.0	95.2	95.7	96.8
	Example 3:	97.2	97.9	98.3	97.0	97.7	98.1
	Example 4:	97.3	98.0	98.6	97.0	97.8	98.3

O_2 gas (1.5×10^{-4} Torr) added during deposition of TiO_2 .

O_2 gas (1.5×10^{-4} Torr) added throughout deposition of Al_2O_3 .

Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 6 (Cont'd)

Degree of vacuum during deposition of Cu ($\times 10^{-5}$ Torr)	Reflectance (S polarized light)					
	Before durability test			After durability test		
	655 nm (%)	780 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)
2.5	Example 1:	95.2	95.9	96.5	94.8	95.6
	Example 2:	95.0	95.8	96.8	94.8	95.5
	Example 3:	95.7	96.6	97.5	94.9	95.9
	Example 4:	95.7	96.7	97.6	94.9	95.8
3.0	Example 1:	94.9	95.7	96.0	94.4	95.4
	Example 2:	94.7	95.5	96.5	94.2	95.2
	Example 3:	95.4	96.5	96.9	94.9	96.2
	Example 4:	95.5	96.4	97.5	94.8	95.9

O₂ gas (1.5×10^{-4} Torr) added during deposition of TiO₂.

O₂ gas (1.5×10^{-4} Torr) added throughout deposition of Al₂O₃.

Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 7

Layer thickness by which no O ₂ gas was added after start of Al ₂ O ₃ deposition	Reflectance (S polarized light)						Adhe- sion	
	Before durability test		After durability test					
	655 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)	780 nm (%)		
O ₂ gas added throughout deposition	Example 1:	96.1	96.3	97.2	96.0	96.3	97.2	A
	Example 2:	95.5	96.1	97.1	95.4	96.3	97.7	A
	Example 3:	97.5	98.0	98.6	97.3	97.8	98.5	A
	Example 4:	97.7	98.2	98.8	97.5	98.1	98.7	A
8% of the stated layer thickness	Example 1:	96.0	96.3	97.2	96.0	96.2	97.1	A
	Example 2:	95.5	96.1	97.1	95.3	96.0	97.0	A
	Example 3:	97.5	98.0	98.5	97.4	97.8	98.4	A
	Example 4:	97.7	98.2	98.8	97.5	98.1	98.7	A
15% of the stated layer thickness	Example 1:	96.5	96.7	97.7	96.4	96.7	97.7	A
	Example 2:	95.8	96.4	97.4	95.7	96.3	97.3	A
	Example 3:	97.8	98.2	98.6	97.7	98.2	98.5	A
	Example 4:	97.8	98.4	98.8	97.7	98.3	98.7	A
23% of the stated layer thickness	Example 1:	96.6	96.7	97.7	96.4	96.5	97.6	A
	Example 2:	95.9	96.5	97.5	95.8	96.4	97.4	A
	Example 3:	97.9	98.2	98.7	97.8	98.1	98.6	A
	Example 4:	97.8	98.4	98.9	97.7	98.3	98.7	A
30% of the stated layer thickness	Example 1:	96.6	96.8	97.8	96.5	96.4	97.7	A
	Example 2:	95.9	96.4	97.4	95.7	96.3	97.4	A
	Example 3:	97.8	98.2	98.6	97.7	98.1	98.5	A
	Example 4:	97.9	98.5	98.9	97.8	98.4	98.8	A

O₂ gas (1.5x10⁻⁴ Torr) added during deposition of TiO₂.
Degree of vacuum before deposition of Cu: 1.0x10⁻⁵ Torr.
Pressure for addition of O₂ gas during deposition of Al₂O₃: 1.5x10⁻⁴ Torr.
Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 7 (Cont'd)

Layer thickness by which no O ₂ gas was added after start of Al ₂ O ₃ deposition	Reflectance (S polarized light)						Adhe- sion	
	Before durability test		After durability test					
	655 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)	780 nm (%)		
33% of the stated layer thickness	Example 1:	96.3	96.6	97.5	96.2	96.4	97.4	C
	Example 2:	95.6	96.2	97.0	95.4	96.0	96.9	C
	Example 3:	97.6	98.0	98.4	97.5	97.9	98.3	C
	Example 4:	97.7	98.1	98.7	97.6	98.0	98.5	C
46% of the stated layer thickness	Example 1:	96.3	96.5	97.5	96.2	96.4	97.4	C
	Example 2:	95.6	96.1	97.0	95.5	96.0	96.9	C
	Example 3:	97.5	98.0	98.5	97.4	97.9	98.4	C
	Example 4:	97.6	98.0	98.7	97.5	97.9	98.6	C
54% of the stated layer thickness	Example 1:	96.2	96.4	97.2	96.0	96.2	97.0	C
	Example 2:	95.5	96.0	96.9	95.4	96.0	96.9	C
	Example 3:	97.4	97.9	98.5	97.3	97.8	98.4	C
	Example 4:	97.5	97.9	98.6	97.4	97.8	98.5	C
62% of the stated layer thickness	Example 1:	96.1	96.3	97.1	96.0	96.2	97.1	C
	Example 2:	95.4	95.9	96.8	95.2	95.6	96.5	C
	Example 3:	97.3	97.7	98.4	97.1	97.5	98.2	C
	Example 4:	97.4	97.8	98.5	97.3	97.7	98.4	C

O₂ gas (1.5x10⁻⁴ Torr) added during deposition of TiO₂.

Degree of vacuum before deposition of Cu: 1.0x10⁻⁵ Torr.

Pressure for addition of O₂ gas during deposition of Al₂O₃: 1.5x10⁻⁴ Torr.

Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 8

Amount of O ₂ gas added during deposition of Al ₂ O ₃ ($\times 10^{-4}$ Torr)	Adhesion
0.0	Example 1: C Example 2: C Example 3: C Example 4: C
0.3	Example 1: C Example 2: C Example 3: C Example 4: C
0.5	Example 1: A Example 2: A Example 3: A Example 4: A
1.0	Example 1: A Example 2: A Example 3: A Example 4: A
1.2	Example 1: A Example 2: A Example 3: A Example 4: A

O₂ gas (1.5×10^{-4} Torr) added during deposition of TiO₂.
Degree of vacuum before deposition of Cu: 1.0×10^{-5} Torr.
O₂ gas (1.5×10^{-4} Torr) added throughout deposition of Al₂O₃.

Table 8 (Cont'd)

Amount of O ₂ gas added during deposition of Al ₂ O ₃ ($\times 10^{-4}$ Torr)	Adhesion
1.5	Example 1: A Example 2: A Example 3: A Example 4: A
2.0	Example 1: A Example 2: A Example 3: A Example 4: A
2.2	Example 1: C Example 2: C Example 3: C Example 4: C
2.5	Example 1: C Example 2: C Example 3: C Example 4: C

O₂ gas (1.5×10^{-4} Torr) added during deposition of TiO₂.
Degree of vacuum before deposition of Cu: 1.0×10^{-5} Torr.
O₂ gas (1.5×10^{-4} Torr) added throughout deposition of Al₂O₃.

Table 9

Corrosion percentage (%)	Film lifting percentage (%)	Reflectance (S polarized light)				Adhe- sion tance	Wiping resis- tance
		Before durability test 655 nm (%)	Before durability test 675 nm (%)	After durability test 780 nm (%)	After durability test 780 nm (%)		
Example: 1	5.2	96.1	96.3	97.2	96.3	97.2	A
2	3.3	95.5	96.1	97.1	95.4	96.3	A
3	3.7	97.5	98.0	98.6	97.3	97.8	A
4	4.0	97.7	98.2	98.8	97.5	98.1	A

Durability test conditions: 70°C, 85%RH, ozone 1 ppm, 100 hrs.

Table 10

Intermediate layer material	Corrosion Number of occurrence/ number of exam.	Per- cent- age (%)	Reflectance (S polarized light)						Adhe- sion
			Before durability test		After durability test				
			655 nm (%)	780 nm (%)	655 nm (%)	675 nm (%)	780 nm (%)		
Cr	125/190	65.8	96.5	96.5	97.2	97.0	97.1	97.0	A
None	13/20	65.0	94.7	95.6	96.7	93.0	94.3	96.6	C
Ni	12/20	60.0	88.4	90.9	95.4	84.3	87.3	92.7	A
Ti	10/20	50.0	95.4	95.7	96.7	93.2	94.2	96.5	A
Ni-Cr(20)	2/20	10.0	96.2	96.5	97.2	96.3	96.5	97.1	A
Cr ₂ O ₃ (with O ₂)	3/60	5.0	85.8	89.1	94.5	82.2	86.6	93.7	A
Cr ₂ O ₃ (without O ₂)	12/60	20.0	94.6	95.9	96.8	94.3	95.4	96.9	A
ZrO ₂ (with O ₂)	7/60	11.7	91.1	94.0	96.3	90.4	92.7	96.7	A
Al ₂ O ₃ (without O ₂)	4/20	20.0	94.7	95.6	96.6	94.0	94.7	96.8	A
SiO ₂ (with O ₂)	7/20	35.0	91.7	93.3	96.0	91.0	93.0	96.4	A
Ta ₂ O ₅ (with O ₂)	8/20	40.0	94.3	95.5	97.0	95.3	96.5	97.0	A
Ta ₂ O ₅ (without O ₂)	11/60	18.3	94.5	95.7	96.9	95.3	96.1	97.0	A
TiO ₂ (with O ₂)	6/180	3.3	95.5	96.1	97.1	95.4	96.3	97.7	A

Table 11

Intermediate layer material	Phenomenon of film lifting		
	Number of occurrence/ number of examination	Percentage (%)	Wiping resistance test
Cr	45/190	23.7	A
None	9/20	45.0	A
Ni	8/20	40.0	A
Ti	7/20	35.0	A
Ni-Cr (20)	6/20	30.0	A
Cr ₂ O ₃ (with O ₂)	0/60	0.0	A
Cr ₂ O ₃ (without O ₂)	0/60	0.0	A
ZrO ₂ (with O ₂)	3/60	5.0	A
Al ₂ O ₃ (without O ₂)	1/20	5.0	A
SiO ₂ (with O ₂)	2/20	10.0	A
Ta ₂ O ₅ (with O ₂)	0/20	0.0	A
Ta ₂ O ₅ (without O ₂)	2/60	3.3	A
TiO ₂ (with O ₂)	0/180	0.0	A